Hydrogen bonding in picolinic acid N-oxide. 
Part II: A proposal for dissipative laser driven proton transfer dynamics

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Abstract
Laser control of proton dynamics in the medium-strong intramolecular hydrogen bond of picolinic acid N-oxide (PANO) is investigated. This work is an extension of our recent article dealing with the “statical” effects of hydrogen bonding in PANO [J. Mol. Struct. (Theochem) 500 (2000) 429–440]. A two-dimensional model potential is extracted from DFT calculations that include the proton transfer motion and the heavy atom mode. The effects of the environmental degrees of freedom were treated by means of their spectral density within the density matrix formalism. The proton dynamics is monitored over time by calculating the nonlinear optical response nonperturbatively in the driving field. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction
Hydrogen bonds are of central importance to the structure and function of biological macromolecules (for recent reviews see Ref. [1]). Numerous experimental and theoretical studies have been carried out in the past few decades to elucidate the dynamics of proton transfer (PT) along intra- or intermolecular hydrogen bonds [2]. In particular, PT taking place in strong (low barrier) hydrogen bonds has attracted considerable attention since the nature of PT reactions in such systems strongly depends on the molecular environment [3–5]. Apart from their biochemical importance, the very short time scale of PT processes make them relevant for femtochemistry studies [6].

Ultrafast laser spectroscopy is a particularly powerful technique [7] for understanding the dynamics of PT reactions in various chemical environments. Recent experiments have shown that the dynamics of OH···O bonds in an isotopic variety of liquid water proceeds on a sub-ps time scale [8]. Takeda et al. estimated the reaction time for the photochromic intramolecular PT in 2-(2′,4′-dimitrobenzyl)pyridine to be in the range of 320–500 fs [9]. The vibrational population dynamics of the OH stretching mode during a condensed phase hydrogen bonding bimolecular reaction has been reported in Ref. [10]. Femtosecond vibrational spectroscopy has also been employed to study solute–solvent interactions as shown in Ref. [11] where the photodissociation

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of an intermolecular hydrogen bond between a coumarin dye and a polar solvent was observed.

On the theoretical side much of the work has been associated with proton dynamics. The proton is a light particle having a de Broglie wavelength of 0.3 Å at room temperature. Therefore, in treating PT processes the quantum nature of the proton has to be taken into account. Another important aspect of modeling PT reactions is the coupling of the proton motion to the motion of the molecular scaffold [12–14]. As an exact quantum description of all 3N – 6 nuclear degrees of freedom is not feasible, considerable attention has been paid to the development of mixed quantum-classical methods [15–34]. On the other hand the density matrix theory (DMT) is a well-established method for treating the dynamics of a small quantum system coupled to a quantum-mechanical environment [35]. If the interaction between the oscillator bath and the system is rather weak, i.e. a perturbational expansion of the system–bath coupling can be carried out, one can take advantage of the Redfield theory [36,37]. Malzahn and May used the Redfield theory in the Markovian approximation to control the state selective excitation of the O–H stretching vibration [38]. In Ref. [39] they also reported an extension of the density matrix formalism to include the field dependence of the Redfield tensor. Korolkov et al. included non-Markovian effects in their simulation of laser controlled HOD vibrational dynamics [40] and isomerization in substituted semibullvalenes [41]. Recently, we investigated the photoinduced PT in thiaoacetylacetone, retaining the Markovian structure of Redfield theory but enlarging the system to include the PT coordinate as well as the strongly coupled O–S stretching mode [42,43]. In contrast, Scheurer and Saalfrank used DMT in the Lindblad formalism to treat double PT in a benzoic acid dimer [44].

In this paper we are concerned with laser driven PT in a strong intramolecularly hydrogen bonded system in solution, i.e. picolinic acid N-oxide (PANO). The nature of the hydrogen bond in PANO is evident from the vibrational spectra in which the OH asymmetric stretching band appears between 1300 and 1600 cm⁻¹, depending on the solvent [45]. Here we will show how state selective vibrational excitation can be used as a means for studying energy and phase relaxation in real time. While experiments on state selective excitation by sub-picosecond IR pulses have been reported for diatomic molecules [46,47], bond selective excitation in polyatomic molecules continues to be a challenge. Since the selective preparation of excited vibrational states requires very intense laser [48–50] fields, a nonperturbative treatment of the nonlinear optical response of the molecular system is required. The purpose of the paper is to investigate the spectroscopic signatures of a laser driven PT in an asymmetric model system and to identify those features in a picosecond time-resolved infrared spectra of PANO that could prove to be characteristic for medium-strong hydrogen bonds in general.

The rest of the paper is organized in the following way. In Section 2 we present the two-dimensional DFT calculated hypersurface for PANO, followed by the introduction of the two-dimensional model Hamiltonian. Section 3 outlines the elements of nonlinear optics necessary for the calculation of nonlinear optical signals. Numerical results of the laser controlled vibrational excitation in PANO, as well as the time-resolved spectra of the model system, are provided in Section 4. The paper is summarized in Section 5.

2. Theoretical model

2.1. DFT results

The calculated proton potential in hydrogen bonded systems is very sensitive to the applied level of theory. There is a general rule that one should use large, flexible basis sets containing a significant number of polarization functions. The proper inclusion of the electron correlation is mandatory if one wants to reproduce the proton potentials [51]. The barrier typically increases with the size of the basis set and decreases with the inclusion of the electron correlation. In intrinsically asymmetric systems like PANO the barrier may be absent and the second minimum can be manifested as an inflection point in the proton potential.
In this work we applied the DFT method including the correlation functional proposed by Becke [52] and the correlation functional proposed by Lee et al. [53] B3LYP together with the basis set 6-31G(d). This split-valence basis set augmented by polarization functions on the heavy atoms is flexible enough to reproduce the proton potentials. We took the O–O distance and the O–H distance into consideration in the construction of the hypersurface. All other degrees of freedom were optimized under the constraint of planarity. We applied the method as implemented in the GAUSSIAN98 [54] program package.

The adiabatic reaction path has been calculated at the B3LYP/6-31G(d) level of theory and it is depicted in Fig. 1. The chosen reaction coordinate is the O–H distance. Although several authors have shown that DF methods provide very low energy barriers for PT processes [55,56] the applied level of theory is a compromise between the computational costs and the reliability of the results. The very preliminary calculation of the hypersurface on the B3LYP/6-31+G(d,p) level is in very close agreement with the present results.

2.2. The Hamiltonian operator

The reaction surface Hamiltonian approach [57] is a well established procedure for deriving the Hamiltonian from DFT data on a reaction surface spanned by few strongly coupled degrees of freedom. The remaining degrees of freedom are treated as local harmonic normal modes. Alternatively an entirely Cartesian formulation of the Hamiltonian is also possible [58]. Recently, Kühn et al. proposed an all Cartesian reaction surface for treating the laser driven PT in a large polyatomic molecule – 8-hydroxyimidazo[1,2-alpyridine [59]. The main advantage of this approach is that any couplings between different coordinates is accounted for in the potential energy part while the kinetic operator is diagonal.

In the present paper we formulate the problem in terms of the generic system–bath Hamiltonian. The advantage of the applied approach is that it allows for quantum treatment of the entire system. Makri and Miller used the system–bath approach to treat the PT in malonaldehyde [13] and in Refs. [42,43] we addressed the question of proton dynamics in an intramolecular hydrogen bond in thioacetylocetone. For the system at hand, PANO, the choice of system coordinates was based on the DFT result from Section 2.1. It turns out that the proton motion can be described by a single Cartesian coordinate x, which is the projection of the H atom position onto the O–O distance. An estimate of the in-plane deformation frequency has been made in Ref. [45] by calculating the proton potential function for the proton in-plane bending. The potential function is nearly parabolic (see Ref. [45], Fig. 5) and the energy levels are only slightly dependent on the O–O distance. This allows us to confine the transversal proton displacement to the bath part of the Hamiltonian.

The influence of the heavy atom stretching mode on the PT coordinate has been pointed out several times [12,60,61]. The DFT data for PANO confirmed that the O–O stretching mode couples strongly to the PT coordinate since it modifies the position of the PT minima as well as the shape of the proton potential. This is in agreement with the indirect mechanism for O–H stretching band broadening, the theory developed by Marechal [62] and Witkowski and Wojcik [63]. While for a short O–O distance (2.37 Å) the proton potential is a slightly asymmetric function, at the equilibrium O–O distance of 2.54 Å the proton potential...
function is strongly asymmetric with an inflection on the NO side. At greater O–O distances the inflection becomes more pronounced. The position of the energy minimum shifts concomitantly from 0.987 to 1.019 Å thus keeping the proton far from the middle of the H-bond.

A two-dimensional PES was constructed through the evaluation of a collection of 165 points corresponding to different O–O and O–H distances. All other geometry parameters are optimized within each calculation. In some extreme cases (e.g. very long or very short O–O distance), the geometry is forced to retain planarity, i.e. the torsion angles are fixed at 0° or 180°. The ranges covered were from 0.8 to 1.8 Å with an increment of 0.1 Å for the O–H distance and from 2.10 to 3.3 Å for the O–O distance with an increment varying from 0.05 Å around the bottom of the PES to 0.15 Å towards the boundary. The lowest energy around the borders of the surface was ≈15.5 kcal mol⁻¹ which was not enough for an accurate evaluation of the high-lying vibrational energy levels that might be involved in the laser driven PT. Therefore, several empirical functions (for a review see Ref. [64]) have been fitted by least squares methods to the available ab initio data. The fitting procedure was carried out by using Mathematica 4. The two-dimensional model potential can be expressed as

\[ V(x, Q) = S_\nu(x) + S_\varphi(Q) + S_{\nu\varphi}(x, Q), \]

(1)

where \( S_\nu(x) \) is the potential energy for the proton motion along the coordinate \( x \), \( S_\varphi(Q) \) is the potential energy for the heavy atom mode and \( S_{\nu\varphi}(x, Q) \) is the coupling function which contains the physics of the interaction between the two modes. The optimal values of the fitting parameters are listed in Table 1. We found that the characteristic behavior of the potential along the PT coordinate is most easily modeled by a fourth-order polynomial function of the form

\[ S_\nu(x) = k_1 \frac{x^2}{2} + k_2 \frac{(x - x_0)^4}{2} + \delta. \]

(2)

The origin of the coordinate system has, notably, been placed at the minimum of the potential. The heavy atom motion is characterized by the Morse potential

<table>
<thead>
<tr>
<th>( S_\nu(x) ) (a.u.)</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
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<td>0.082</td>
<td>1.11</td>
<td>0.98</td>
<td>0.018</td>
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</tbody>
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Table 1

Optimal values of the fitting parameters in atomic units for the two-dimensional model potential: Eqs. (2–4)

\[ S_\varphi(Q) = D(1 - e^{\alpha(Q - Q_0)})^2. \]

(3)

By comparison with available DFT data we found that the energetics of the PANO system can more accurately be reproduced by the following coupling function:

\[ S_{\nu\varphi}(x, Q) = \alpha xQ + \beta x^2 Q + \gamma xQ^2. \]

(4)

Therefore the total system Hamiltonian is given by

\[ H_S = \frac{p_x^2}{2\mu_x} + \frac{p_Q^2}{2\mu_Q} + V(x, Q), \]

(5)

where \( \mu_x \) and \( \mu_Q \) are the reduced masses for the respective motions. The geometry was allowed to relax at each point of the PES making the assignment of the masses unclear. Here we used \( \mu_x = 1.05 \) and set the reduced mass of the O–O coordinate to \( \mu_Q = 16.0 \) in order to approximately reproduce the PANO frequencies [45]. The two-dimensional model potential surface for PANO is shown in Fig. 2, together with the eigenfunctions \( \phi_\nu \) of \( H_S \). The eigenfunctions and eigenvalues were obtained using the Fourier grid Hamiltonian method [65].

Let us now examine the eigenfunctions in some detail. The functions \( \phi_0 - \phi_6 \) are delocalized along the heavy atom mode while the \( \phi_7 \) state is the first state delocalized in the PT direction. More important from the point of view of laser driven PT are the delocalized states lying close to the plateau region, particularly the \( \phi_9 \) and \( \phi_{10} \) states. Although there is no minimum on the N-oxide side of the potential the \( \phi_{10} \) has a significant localization of probability density on this side. The effect can be understood in terms of the JWKB approxi-
mation in which the probability is proportional to the momentum of the particle.

In addition to the molecular Hamiltonian, the interaction of the system \( H_S \) with the external field needs to be specified in order to describe the laser driven dynamics. Within the semiclassical dipole approximation the field–matter Hamiltonian reads

\[
H_{\text{F}}(t) = -d(x, Q)E(t),
\]

where \( d(x, Q) \) is the dipole operator. For PANO the dipole function has been obtained by interpolation of DFT data in the range \( 0.8 \leq x \leq 1.8 \) Å, \( 2.35 \leq Q \leq 3.10 \) Å. The dipole moment changes from 2.34 to 3.7 D when going from the carboxylic to the N-oxide side. Outside this region the dipole function is taken to be constant.

Finally, we consider the model environment i.e. the large number of intramolecular modes as well as the possible solvent modes that have been neglected so far. For simplicity we will take the solvent to be nonpolar and nonhydrogen bonding. In Refs. [60,61] the coupling of some selected degrees of freedom on the proton motion has been explicitly treated in terms of mixed classical-quantum dynamics. Here we will use the relaxation theory and model the environment as a set of harmonic oscillators

\[
H_B = \sum_i \left( \frac{p_{i,B}^2}{2M_{i,B}} + \frac{k_{i,B}q_{i,B}^2}{2} \right),
\]

The bath oscillators are bilinearly coupled to both system degrees of freedom by

\[
H_{SB} = \sum_i (c_{i,x} x + c_{i,Q} Q) q_{i,B}.
\]

For simplicity we use the same coupling \( c_i \) for both system coordinates. The influence of higher-order terms in the expansion of the system–bath coupling is given in Ref. [66]. Treating the system–bath interaction perturbatively to second-order and assuming Markovian dynamics, the rates for vibrational energy relaxation and coherence dephasing can be obtained [35]. In the framework of the discussed approximations all information about the system–bath coupling is contained within the spectral density. We assume the following empirical form for \( J(\omega) \) which is typical for a condensed phase environment having a broad spectrum [35]

\[
J(\omega) = \frac{g}{\omega_k} \frac{\omega}{\omega_k} \text{e}^{-|\omega|/\omega_k},
\]

where the coupling strengths \( |c_i|^2 \) in the factor \( g \) have been absorbed. For the system under

Fig. 2. The two-dimensional potential energy surface, Eq. (1), is shown together with the density plots for some of the vibrational (\( \nu \)) eigenstates of the system Hamiltonian \( H_S \). From left to right and top to bottom we have \( \nu = 0, 1, 7 \) and 10.
consideration we take $J_{\nu}$ to be at its peak at the characteristic frequency $\omega_c = 1100$ cm$^{-1}$ in order to stress the influence of the C–O stretching vibration [61] on the O–H–O fragment dynamics.

3. Transient absorption spectroscopy

The dynamics of the PT system embedded in a dissipative environment is determined by the reduced density operator $\hat{\rho}$. In the numerical application a specific representation for $\hat{\rho}$ has to be chosen. As we are interested in preparing the system in a selected vibrational state the eigenstates representation of $\hat{\rho}$ is the most appropriate. The reduced density matrix $\rho_{\nu\nu'}$ in the state representation is defined as

$$\hat{\rho} = \sum_{\nu,\nu'} \rho_{\nu\nu'} |\nu\rangle \langle \nu'|$$  \hspace{1cm} (9)

and the equations for the elements of the density matrix read:

$$\frac{d\rho_{\nu\nu'}}{dt} = -i \omega_{\nu\nu'} \rho_{\nu\nu'} + i \delta(t) \sum_{\nu''} (d_{\nu\nu''} \rho_{\nu''\nu'} - d_{\nu''\nu'} \rho_{\nu\nu''})$$

\[- \sum_{\nu''} R_{\nu\nu''\nu'} \rho_{\nu''\nu'}; \hspace{1cm} (10)\]

where $\omega_{\nu\nu'} = (E_{\nu} - E_{\nu'})/\hbar$ are the transition frequencies between different eigenstates of the system. The Hamiltonian $H_S$ and $d_{\nu\nu'}$ are the matrix elements of the dipole operator. The dissipative dynamics is accounted for in the Redfield relaxation tensor $R_{\nu\nu''\nu'}$ (see for example Ref. [35]), which contains, in addition to the spectral density $J(\omega)$, the matrix elements of $H_{SB}$. The details of the numerical propagation of the Redfield equations have been given in Ref. [42].

Let us now provide the link between the reduced density matrix and the observables of nonlinear optical spectroscopy. The theoretical work on the subject, mainly by Mukamel, is based on the expansion of the density operator in a power series of the electric field [67]. In the specific situation at hand we will model a pump–probe type experiment in which the first pump pulse prepares the system in a nonstationary state while its time evolution is interrogated by a weak probe pulse at different delay times from the pump. Since the selective preparation of excited vibrational states is only achieved using very intense laser fields, often in the $10^{12}$ W cm$^{-2}$ range the perturbative treatment of field–matter interaction is not convenient. The lowest-order perturbation theory is adequate only for the treatment of the weak probe field in which transient absorption is measured. The nonperturbative treatment of the interaction with the external field can be most easily achieved by numerical propagation of the Redfield equations (Eq. (10)) thus yielding the polarization $P(t)$. The polarization, i.e. the expectation value of the dipole operator, is the fundamental unit in the theoretical treatment of nonlinear optical spectroscopy. It is given by

$$P(t) = N_{\text{mol}} \text{tr}_{\text{sys}} \text{d}\rho(t), \hspace{1cm} (11)$$

where $N_{\text{mol}}$ is the density of the polarizable molecules in the sample. Note that an overall polarization signal is thus calculated. One cannot distinguish between the different spectroscopic techniques associated with the different directions of the wave vector $k$ of the emitted radiation [68]. Here we are interested in the part of the polarization which travels in the probe field direction. As pointed out in Ref. [68] in a pump–probe experiment using a low-intensity probe and with nonoverlapping pump and probe this contribution is often dominant. Therefore, we will assume that as a reasonable approximation we can neglect the phase problem [43,69].

In a pump–probe experiment the external field is given as the sum of two components

$$E(t) = E_p(t)e^{-i\omega_p t} + E_i(t)e^{-i\omega_i t} + \text{c.c.}, \hspace{1cm} (12)$$

where $E_{p,i}(t)$ is the envelope of the pump–probe field and $\omega_{p,i}$ is the pump–probe carrier frequency. The time-integrated probe pulse absorption $S_{\text{tot}}(\omega, \tau)$ can be calculated by considering the mean energy loss of the probe passing through the sample. Since ultrashort IR probe pulses are used, the temporal variation of the probe field envelope
should be taken into account. The total pulse absorption is then given by [43]

$$S_{\text{tot}}(\omega_1, \tau) = \int dt \left( 2\omega_1 \text{Im} [E^*_i(t)P_i(t)] - 2 \text{Re} \left[ \frac{dE^*_i(t)}{dt} P_i(t) \right] \right), \quad (13)$$

where $P_i(t)$ is the envelope of the polarization and we indicated that the signal depends on the delay time $\tau$ between the pump and the probe. Additional information about the system can be gained by decomposing the transmitted light in the spectrometer. The appropriate signal to be calculated is then

$$S_{\text{disp}}(\omega, \tau) = 2(\omega_1 + \omega) \text{Im} [E^*_i(\omega - \omega_1)P_i(\omega - \omega_1)], \quad (14)$$

where the Fourier transform of the envelopes of the pump pulse

$$E_i(\omega - \omega_1) = \frac{1}{2\pi} \int dt e^{i(\omega - \omega_1)t} E_i(t), \quad (15)$$

and of the polarization

$$P_i(\omega - \omega_1) = \frac{1}{2\pi} \int dt e^{i(\omega - \omega_1)t} P_i(t) \quad (16)$$

are included. The total and the dispersed absorption signal are related by

$$S_{\text{tot}}(\omega_1, \tau) = \int d\omega S_{\text{disp}}(\omega, \tau). \quad (17)$$

In Section 4 we will consider the dispersed signal of the form

$$S(\omega, \tau) = S^{(p+1)}_{\text{disp}}(\omega, \tau) - S^{(1)}_{\text{disp}}(\omega, \tau) \quad (18)$$

which is defined as the probe absorption in the presence of the pump pulse $S^{(p+1)}_{\text{disp}}$ minus the probe absorption in the absence of the pump $S^{(1)}_{\text{disp}}$. Note that the dispersed signal $S_{\text{disp}}$ is calculated by propagating the reduced density matrix twice, i.e. with both pulses and with the pump pulse alone, and then subtracting the result. It is given by

$$P_i(t) = N_{\text{molecule}} e^{i\omega_1 t} \sum_{m'\sigma'} d_{m'\sigma'} \left[ \rho^{(p+1)}_{m'\sigma'}(t) - \rho^p_{m'\sigma'}(t) \right]. \quad (19)$$

### 4. Results

#### 4.1. Linear absorption

In the following section, we consider the system to be in thermal equilibrium at 300 K and use a moderate coupling to the bath $g = 8 \times 10^{-5}$. To capture the basic features of the PANO system we calculated the linear absorption spectrum. The absorption signal of a weak probe is given by

$$S^{(1)}_{\text{disp}}(\omega) = 2(\omega_1 + \omega) \text{Im} [E^*_i(\omega - \omega_1)\tilde{P}_i(\omega - \omega_1)], \quad (20)$$

where the polarization $\tilde{P}_i(\omega - \omega_1)$ contains only the probe field ($E_p = 0$). For the numerical propagation we have chosen an ultrashort Gaussian probe pulse of only 20 fs having a full-width at a half-maximum of 530 cm$^{-1}$. In order to characterize the lower part of the PANO potential the carrier frequency of the probe was tuned to $\omega_1 = 500$ cm$^{-1}$. The linear absorption signal is shown in Fig. 3. The dominant transition occurring at 308 cm$^{-1}$ corresponds to the $\phi_0 \rightarrow \phi_1$ heavy mode excitation. As we start from a state initially in thermal equilibrium (at 300 K the first seven states have occupation probabilities higher than $10^{-5}$) one can notice that the feature around 308 cm$^{-1}$ actually corresponds to a number of transitions: $\phi_3 \rightarrow \phi_2$, $\phi_2 \rightarrow \phi_1$, $\phi_0 \rightarrow \phi_1$. A similar progression found around 615 cm$^{-1}$ corresponds to the $\phi_2 \rightarrow \phi_4$, $\phi_1 \rightarrow \phi_3$, $\phi_0 \rightarrow \phi_2$ transitions, while the signal at 920 cm$^{-1}$ is due to the $\phi_2 \rightarrow \phi_5$, $\phi_1 \rightarrow \phi_4$, $\phi_0 \rightarrow \phi_5$ transitions. Furthermore, a low-intensity line corresponding to the above shelf $\phi_7 \rightarrow \phi_{10}$ transition is found at 480 cm$^{-1}$.

We then calculated the linear absorption signal for a probe pulse with carrier frequency $\omega_1 = 2000$ cm$^{-1}$. The height frequency part of the spectrum (lower panel Fig. 3) is dominated by the $\phi_0 \rightarrow \phi_7$ transition (1933 cm$^{-1}$) corresponding to the excitation of OH stretching mode. The close signal at 1925 cm$^{-1}$ is due to the $\phi_1 \rightarrow \phi_9$ transition. The $\phi_1 \rightarrow \phi_{10}$ transition (2105 cm$^{-1}$) and the $\phi_0 \rightarrow \phi_9$ signal (2234 cm$^{-1}$) are also present. The frequencies of several other transitions are indicated in the figure captions.
4.2. Laser control

This section focuses on monitoring the laser controlled excitation of the asymmetric $\phi_{10}$ vibrational eigenstate of PANO. As the signal corresponding to the $\phi_0 \rightarrow \phi_{10}$ transition does not occur in the linear absorption spectrum direct excitation of the $\phi_{10}$ state will probably require very high field intensities. This suggests that an indirect pathway via the delocalized $\phi_7$ state is more efficient for achieving the population switch. To obtain the laser pulses parameter for the
\( \phi_0 \rightarrow \phi_7 \rightarrow \phi_{10} \) excitation we consider our model system to be a series of two-level systems. From the theory of two-level systems one gets that for a resonant transition a complete inversion of population occurs when the pulse area is equal to \( \pi \) [70]. Employing two overlapping 1R pump pulses of duration \( t_{p1} = 750 \) fs and \( t_{p2} = 700 \) fs, each having a Gaussian shape with widths \( \Delta_{p1/p2} = t_{p1/p2}/4 \),

\[
E(t) = E_{0,p1} \left( \frac{2}{\pi \Delta_{p1}^2} \right)^{1/2} \exp \left[ -2\left(t - t_{p1}\right)^2/\Delta_{p1}^2 \right] \\
\times \cos(\omega_{p1}t) + E_{0,p2} \left( \frac{2}{\pi \Delta_{p2}^2} \right)^{1/2} \exp \left[ -2\left(t - t_{p2}\right)^2/\Delta_{p2}^2 \right] \cos(\omega_{p2}t),
\]

(21)

and at near resonant carrier frequencies \( \omega_{p1/p2} \) one ends up with the following field amplitudes \( E_{0,p1} = 0.00155 \) a.u., \( E_{0,p2} = 0.0024 \) a.u. The total duration of the pulses is \( t_d = (t_{p1} + t_{p2}) - \tau = 1050 \) fs, with \( \tau = 400 \) fs being the overlapping time. In order to compete efficiently against energy and phase relaxation we have chosen a maximum overlapping time that still allows for a good level of controllability in the dissipation-free case. Note that the field parameters obtained in the dissipation-free case were not reoptimized after inclusion of the dissipation. The resulting laser field (inset), together with the population dynamics under dissipative condition of all states involved in the excitation process, is displayed in Fig. 4. Inspection of the population dynamics shows that a considerable level of controllability has been achieved. At the end of the second pulse we have a significant switch of population between the \( \phi_0 \) and the \( \phi_{10} \) state with a reaction yield of \( Y = 0.75 \). After the end of the pulse the relaxation inevitably takes the system back to thermal equilibrium. Apparently the relaxation dynamics goes predominantly through the \( \phi_0 \) and \( \phi_7 \) states to get to the equilibrium, while states having excitation in the heavy atom mode do not participate significantly. This particular relaxation pattern is partially a consequence of the bilinear type of system–bath coupling that we used (see Eq. (7)).

Increasing the system–bath coupling constant to \( g = 3 \times 10^{-4} \) reduces the lifetime of the target state to \( \tau_{10} = 300 \) fs (\( \tau_{10} = 1.1 \) ps for \( g = 8 \times 10^{-5} \)). Having the lifetime shorter than the pulse duration destroys the selectivity of the excitation. Although a significant population of the intermediate \( \phi_7 \) state is achieved, relaxation into lower states is much more effective than the \( \phi_7 \rightarrow \phi_{10} \) excitation. The population dynamics for the states involved in the excitation/relaxation processes is shown in the lower panel of Fig. 4.

We will now employ the formalism presented in Section 3 to monitor the photoinduced dynamics in real time. In the following section we will model two types of signals. The simpler signal is the total pump–probe signal obtained according to (Eq. (13)). Excitation is performed by the pump pulse of Fig. 4. The test pulse is a 200 fs Gaussian probe pulse resonant to the \( \phi_7 \rightarrow \phi_{10} \) transition (480 cm\(^{-1}\)). In Fig. 5 we show the total pump–probe absorption in the case of fast relaxation. First, an induced absorption is observed (upper panel of Fig. 5) (positive signal, excited state absorption), followed by a transient bleaching in the time interval after the action of the second pump pulse. The second pump pulse populates the target state causing a sudden change in the total probe absorption (negative signal). After the pump pulse is over an induced absorption is observed due to population relaxation into the \( \phi_7 \) state.

Setting the test pulse carrier frequency in resonance to the \( \phi_0 \rightarrow \phi_7 \) transition (1890 cm\(^{-1}\)) produces a different view of the dynamics. The signal is negative (ground state bleaching) due to population pumping into the \( \phi_7 \) and \( \phi_{10} \) states. The action of the first pump pulse induces a rapid reduction of the absorption. At \( t = 500 \) fs, a change in the behavior of the signal can be seen indicating a temporal de-population of the \( \phi_7 \) due to pumping into \( \phi_{10} \). After the pump pulse is switched off the system relaxes to equilibrium causing the signal to decay. With the present system–bath coupling the thermal equilibrium is reached after some tens of picoseconds. So far, a low-order bilinear expansion of the system–bath interaction Hamiltonian has been assumed, but it is worth investigating how higher-order terms influence the total absorption signal. The dashed line in Fig. 5 represents the total absorption signal.
Fig. 4. The laser field for the selective preparation of the $\phi_{10}$ state via the $\phi_0 \rightarrow \phi_7 \rightarrow \phi_{10}$ pathway is shown in the inset. The laser pulse is a superposition of two overlapping ($\tau = 400$ fs), resonant IR laser pulses with parameters: $E_{0,p1} = 0.00155 \ E_0 \ (e\alpha_b)^{-1}$, $t_{p1} = 750$ fs, $E_{0,p2} = 0.0024 \ E_0 \ (e\alpha_b)^{-1}$, $t_{p2} = 700$ fs. Population dynamics for the driving pulse shown in the inset (solid: $\phi_0$, $\phi_{10}$; dashed: $\phi_7$, $\phi_8$). In the upper panel the system–bath coupling strength is taken to be $g = 8 \times 10^{-3}$ (lifetime of $\phi_{10}$ $\tau_{10} \approx 1$ ps). In the lower panel $g = 3 \times 10^{-4}$ ($\tau_{10} \approx 250$ fs).

calculated upon inclusion of the quadratic term $\propto xQq_1$ into $H_{SB}$. To compare different ways of system–bath coupling we normalized the overall coupling strength [66]. A comparison of the two signals highlighted a faster decay of the total absorption for the quadratic coupling. This is due to the fact that the inclusion of the quadratic term leads to a more efficient mixing of the PT and the heavy atom mode which results in a faster relaxation of the intermediate $\phi_7$ state.
Fig. 5. The total signal, according to Eq. (17), as a function of the delay time between the pump (Fig. 4) and the test pulse. The width of the test pulse is $\Delta t = 200$ fs and the amplitude is 50 times smaller than the pump pulse amplitude. The carrier frequencies are $\omega_1 = 480$ cm$^{-1}$ (upper panel) and $\omega_1 = 2000$ cm$^{-1}$ (lower panel).

We then simulated the dispersed pump–probe signal for PANO. This provides a more global view of the dynamics compared to the total pump–probe absorption. The dynamics for the pump pulse of Fig. 4 is probed with a low frequency $\omega_1 = 200$ cm$^{-1}$ Gaussian test pulse. We used an ultrashort test pulse $\tau_t = 20$ fs where spectral width is sufficient to provide information about the shelf part of the potential where the most interesting transitions take place. The dispersed signal for a slow relaxation in a series of delay times (see figure captions) is shown in Fig. 6. As expected, the dominant feature is the reduced absorption (ground state bleaching) at 308 cm$^{-1}$ which is the result of the depopulation of the ground state. Compared to the linear spectrum of Fig. 3 a
Fig. 6. The dispersed pump-probe signal calculated according to Eq. (14) for the pump pulse shown in Fig. 4. The width of the test pulse is $\Delta t = 20$ fs, the amplitude is 50 times smaller than the pump pulse amplitude and is centered at $\omega_h = 200$ cm$^{-1}$. The system–bath coupling strength is $g = 8 \times 10^{-5}$ (upper panel) and $g = 3 \times 10^{-4}$ (lower panel). The delay times are: $-75, 125, 325, 525, 925, 1525$ fs (from bottom).

number of new lines appeared due to pumping in the above shelf portion of the potential. The feature around 160 cm$^{-1}$ corresponding to the $\phi_9 \rightarrow \phi_{10}$ transition is of particular interest. The position of the line is an indication of the change of the level spacing characteristic for shelf potentials (see Fig. 1). The time evolution of the line indicates an initial increased population of the $\phi_{10}$ state (negative signal, reduced absorption) and a subsequent change of the line shape to an absorption profile because of relaxation into the $\phi_9$ state. After 2 ps there is a decay of the absorption signal. Similarly, a reduced absorption is found for $\phi_7 \rightarrow \phi_{10}$ at 480 cm$^{-1}$ and for $\phi_7 \rightarrow \phi_{11}$ at 506
cm\(^{-1}\). Here there is an obvious distortion of the line shape for overlapping pulses caused by the dynamical Stark shift effect. After the pump pulse is switched off the signal decays due to vibrational and phase relaxation. The dynamics of the target state can also be followed at 351 cm\(^{-1}\) where the \(\phi_{10} \rightarrow \phi_{15}\) transition causes an increase in absorption. Additional insight into the population dynamics is obtained by comparing the time evolution of different peaks. While the signal for the \(\phi_9 \rightarrow \phi_{10}\) transition changes from negative to positive in the time period we monitored, the signal for the \(\phi_7 \rightarrow \phi_{10}\) transition remains negative suggesting a slow depopulation of the \(\phi_7\) state. Increasing the coupling to \(g = 3 \times 10^{-4}\) changed the time evolution of the different peaks. A fast relaxation of the target state results in an increased probe absorption for the \(\phi_9 \rightarrow \phi_{10}\) transition even for very short delay times. The positive signal (excited state absorption) for the \(\phi_{10} \rightarrow \phi_{15}\) transition decreases very quickly. As expected, a faster relaxation induces a change in the dynamics of the \(\phi_7 \rightarrow \phi_{10}\) (480 cm\(^{-1}\)) transition: from reduced absorption at short delay times to increased absorption due to relaxation into the \(\phi_7\) state. After 2 ps the relaxation into lower states causes the absorption signal to decrease.

Finally, the dispersed signal simulation allowed us to determine new pathways for selective vibrational excitation. The signal at 160 cm\(^{-1}\) corresponding to the \(\phi_9 \rightarrow \phi_{10}\) (160 cm\(^{-1}\)) transition indicates a strong coupling between the two states that could be exploited under a different laser control strategy. Although the field intensity required for the indirect \((\phi_0 \rightarrow \phi_9)\) excitation of the \(\phi_9\) state is very high \((E_{0,p1} = 0.0052\) a.u.) it is reduced to \(E_{0,p1} = 0.0014\) a.u. if the system is initially prepared in the first excited state (heavy atom mode). This suggests that vibrationally assisted PT should be considered when looking for new laser control scenarios.

5. Concluding remarks

We investigated the laser driven PT in PANO within a two-dimensional Cartesian reaction surface model. The not explicitly treated degrees of freedom have been modeled by means of their spectral density within the DMT. The two-dimensional hypersurface (O–O and O–H stretchings) together with the dipole moment values have been obtained using medium high level DFT calculations B3LYP/6-31G(d). The maximum of the spectral density was chosen to coincide with the C–O stretching vibration which, by comparison with various scaffold modes, coupled most strongly with the system. Numerical simulation of the linear absorption spectra has been used to propose a two-step strategy for laser controlled state selective excitation of PANO. The first pulse induces a population switch between the ground state and the delocalized \(\phi_7\) state while the second one induces a transition to the \(\phi_{10}\) state that is significantly localized on the N-oxide side. It has been shown that a nonequilibrium population of the selected vibrational state might be established if the lifetime of the selected level were comparable to the laser pulse duration. In other words, dissipation should be slow relative to the laser pulse duration. In a typical condensed phase situation these lifetimes lie in the sub-picosecond region (i.e. fast relaxation rate in our simulation) therefore limiting the selective state preparation to the gaseous phase. However, our study of the influence of the solvent on the PANO potential [45] indicates formation of a second minimum on the N-oxide side.

The laser driven dynamics was characterized by calculating the nonlinear optical response non-perturbatively in the driving field. It has been shown that laser driven PT can be monitored either by the total or the dispersed pump–probe signal. In the dispersed signal we observed an enhanced/reduced (slow/fast relaxation) absorption at a frequency lower than the fundamental frequency. This reflects the presence of a shelf in the potential characteristics for medium-strong hydrogen bonded systems. In conclusion we would like to say a few words about the approximations that have been used in our approach to dissipative dynamics. First, the phase problem that we neglected in the pump–probe simulation can be overcome by introducing a carrier wave expansion of the reduced density matrix, thus allowing for the differentiation of various spectroscopic techniques.
Second, the perturbative treatment of most intramolecular degrees of freedom is the most problematic approximation. In our forthcoming work we will enlarge the quantum system by inclusion of the in-plane hydrogen bending mode and treat the remaining intramolecular degrees of freedom and solvent explicitly using mixed quantum-classical simulation.

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References